

PTO 09-4901

CC=JP
DATE=19980623
KIND=KOKAI
PN=10168245

POLYETHYLENE RESIN COMPOSITION FOR EXTRUSION LAMINATE, AND
EXTRUSION LAMINATE PRODUCT THEREOF

[oshidashi ramineeto-you poriechiren-kei jushi soseibutsu
oyobi sono oshidashi ramineeto hin]

TERADA JUNICHI et al

UNITED STATES PATENT AND TRADEMARK OFFICE
WASHINGTON, D.C. MAY 2009
TRANSLATED BY SCHREIBER TRANSLATIONS, INC.

PUBLICATION COUNTRY	(10):	JP
DOCUMENT NUMBER	(11):	10168245
DOCUMENT KIND	(12):	KOKAI
PUBLICATION DATE	(43):	19980623
APPLICATION NUMBER	(21):	0833184
APPLICATION DATE	(22):	19961212
INTERNATIONAL CLASSIFICATION	(51):	C08L 23/06, C08K 3/34, 5/13, 5/20, 5/524
PRIORITY COUNTRY	(33):	N/A
PRIORITY NUMBER	(31):	N/A
PRIORITY DATE	(32):	N/A
INVENTOR(S)	(72):	TERADA JUNICHI, MORITA TATSUYA, YOSHII NAOHARU
APPLICANT(S)	(71):	ASAHI CHEM IND CO LTD
DESIGNATED CONTRACTING STATES	(81):	N/A
TITLE	(54):	POLYETHYLENE RESIN COMPOSITION FOR EXTRUSION LAMINATE, AND EXTRUSION LAMINATE PRODUCT THEREOF
FOREIGN TITLE	[54A]:	oshidashi ramineeto- you poriechiren-kei jushi soseibutsu oyobi sono oshidashi ramineeto hin

CLAIMS

Claim 1: A polyethylene resin composition for an extrusion laminate,

comprising two or more types of linear low-density ethylene copolymer (An) and two types of low density polyethylene (Bm), wherein

said linear low-density ethylene copolymers (An) are copolymers of ethylene and a C₃₋₂₀ alpha-olefin polymerized with a metallocene compound as catalyst,

one type (A1) of said two or more types of linear low-density ethylene copolymer (An) has a density of 0.87 g/cm³ or less and a melt flow rate of 0.1 to 40 g/10 min,

the other linear low-density ethylene copolymer(s) (An-A1) excluding (A1) has a density greater than 0.87 g/cm³ and a melt flow rate of 0.1 to 40 g/10 min,

one type (B1) of said two types of low density polyethylene has a density of 0.91 to 0.93 g/cm³ and a melt flow rate of 0.1 to 30 g/10 min,

the other type (B2) of said two types of low density polyethylene has a density of 0.91 to 0.93 g/cm³ and a melt flow rate of 1 to 30 g/10 min, and furthermore

¹ Numbers in the margin indicate pagination in the foreign text

the blending rate of An is 50 to 99 wt.% and the blending rate of Bm is 50 to 1 wt.%,

the blending ratio (weight ratio) $\{A1/(An-A1)\}$ of A1 and (An-A1) is from 1/99 to 99/1, and

the blending ratio (weight ratio) (B1/B2) of B1 and B2 is from 99/1 to 1/99.

Claim 2: The A polyethylene resin composition for an extrusion laminate according to claim 1, containing 0.01 to 0.5 parts weight of a phenolic heat stabilizer and/or a phosphorus-based heat stabilizer, 0.01 to 0.2 parts weight of a slip agent, and 0.01 to 2 parts weight of an anti-blocking agent, relative to 100 parts weight of An and Bm combined.

Claim 3: An extrusion laminate product, which has as a sealant layer the polyethylene resin composition for an extrusion laminate according to claims 1 or 2, wherein temperature dependence of heat seal strength is 1.5 or less, heat seal strength is 1.5 kg/15 mm or more, the processability index of the laminate is 2 or more, and drawdown is 80 m/min or more.

DETAILED DESCRIPTION OF THE INVENTION

[0001]

INDUSTRIAL FIELD OF APPLICATION: This invention relates to a polyethylene resin composition for an extrusion laminate. More specifically this invention relates to a polyethylene resin composition for an extrusion laminate suitable for use as a sealant layer for food packaging materials and the like, which maintains the low-temperature sealability and high heat-seal strength of a linear low-density ethylene copolymer obtained by polymerization with a metallocene compound catalyst, and further exhibits stable sealability over a wide temperature range, is excellent in processability and has good slipping properties when an extrusion laminate. The invention further relates to extrusion laminate products thereof.

[0002]

PRIOR ART: Conventionally, low-density polyethylene or ethylene-vinyl acetate copolymer has been used as the polyethylene resin or resin composition for an extrusion laminate intended as a sealant layer. Use has also been made of linear low-density polyethylene as well as resin formed by blending low-density polyethylene with an ethylene-

propylene copolymer. However, these resins have the following disadvantages as well as advantages.

[0003] Although low-density polyethylene has excellent processability, the sealing properties such as heat seal strength and hot tack of this polyethylene, and of ethylene vinyl acetate copolymers, are inferior to those of linear low-density polyethylene. On the other hand, linear low-density polyethylene has poor processability as an extrusion laminate and in some cases has inferior low-temperature sealability when compared to ethylene-vinyl acetate copolymers.

[0004] Thus these resins or resin compositions do not satisfactorily balance processability and the other stringent demands required in, for example, high-speed filling, such as low-temperature sealability, high heat-seal strength and stable heat sealability over a wide temperature range, as well as properties related to filling suitability. These resins cannot therefore be regarded as suitable for an extrusion laminate intended as a sealant layer. Recently, in response to this situation, Japanese Unexamined Patent Application Publication Nos. H8-41254 and H8-188681 have proposed methods for improving the performance of resins for

extrusion laminates intended for a sealant layer, by using a linear low-density polyethylene obtained by copolymerization with a metallocene catalyst.

[0005] However, in these methods, although it is stated that, because of polymer properties originating in aspects of the molecular structure of the linear low-density polyethylene, such as narrow copolymer resin distribution relative to molecular weight, the use of said linear low-density polyethylene as a constituent of the resin composition for an extrusion laminate for a sealant layer results in an improvement in such seal properties as low-temperature sealability, heat seal strength and hot tack, in fact the effect is not substantially adequate. In addition, there have been no clear proposals on methods for resolving problems in the processing of extrusion laminates, such as the large neck-in and low drawdown of linear low-density polyethylene. Nor have methods been disclosed for improving slip properties during filling.

[0006] These methods therefore cannot be said to simultaneously satisfy to a sufficient degree the important characteristics required for the practical use of a resin for an extrusion laminate intended for a sealant layer, such

as slip properties, seal properties and processability of the extrusion laminate.

[0007]

PROBLEM TO BE SOLVED BY THE INVENTION: The present invention was developed in light of the above-described situation, and has as its objective the provision of a polyethylene resin composition for an extrusion laminate suitable for use as a sealant layer for food packaging materials and the like, which exhibits low-temperature sealability, high heat-seal strength and stable heat sealability over a wide temperature range, is excellent in processability and has good slip properties; and the provision of extrusion laminate products thereof.

/3

[0008]

MEANS FOR SOLVING THE PROBLEM: As the result of intensive research into the development of a polyethylene resin composition for an extrusion laminate suitable for use as a sealant layer, which exhibits low-temperature sealability, high heat-seal strength and stable heat-sealability over a wide temperature range, is excellent in processability and has good slip properties, the present inventors et al

arrived at this invention after discovering that said objective could be met by using two or more types of linear low-density ethylene having specific densities and melt flow rates and obtained by polymerization with a metallocene compound as catalyst, blending same at a specific ratio with two types of low-density polyethylene having specific densities, melt flow rates and melt tensions and obtained by, for example, high-pressure radical polymerization, and further adding a heat stabilizer(s), slip agent and anti blocking agent.

[0009] Thus, the first invention is a polyethylene resin composition for an extrusion laminate, comprising two or more types of linear low-density ethylene copolymer (An) and two types of low density polyethylene (Bm), wherein said linear low-density ethylene copolymer (An) is a copolymer of ethylene and a C₃₋₂₀ alpha-olefin polymerized with a metallocene compound as catalyst, one type (A1) of said two or more types of linear low-density ethylene copolymer (An) has a density of 0.87 g/cm³ or less and a melt flow rate of 0.1 to 40 g/10 min, the other linear low-density ethylene copolymer(s) (An-A1) excluding (A1) has a density greater than 0.87 g/cm³ and a

melt flow rate of 0.1 to 40 g/10 min,
one type (B1) of said two types of low density polyethylene has a density of 0.91 to 0.93 g/cm³ and a melt flow rate of 0.1 to 30 g/10 min,
the other type (B2) of said two types of low density polyethylene has a density of 0.91 to 0.93 g/cm³ and a melt flow rate of 1 to 30 g/10 min, and furthermore
the blending rate of An is 50 to 99 wt.% and the blending rate of Bm is 50 to 1 wt.%,
the blending ratio (weight ratio) {A1/(An-A1)} of A1 and (An-A1) is from 1/99 to 99/1, and
the blending ratio (weight ratio) (B1/B2) of B1 and B2 is from 99/1 to 1/99.

[0010] The second invention is a polyethylene resin composition for an extrusion laminate according to the first invention, containing 0.01 to 0.5 parts weight of a phenolic heat stabilizer and/or phosphorus-based heat stabilizer, 0.01 to 0.2 parts weight of a slip agent, and 0.01 to 2 parts weight of an anti-blocking agent, relative to 100 parts weight of An and Bm combined.

[0011] The third invention is an extrusion laminate product, which has as a sealant layer the polyethylene resin

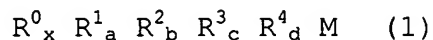
composition for an extrusion laminate according to the first or second inventions, wherein temperature dependence of heat seal strength is 1.5 or less, heat seal strength is 1.5 kg/15 mm or more, the processability index of the laminate is 2 or more, and drawdown is 80 m/min or more.

[0012] The present invention is described in detail below. The linear low-density ethylene copolymers (An) used in this invention are random copolymers of ethylene and a C₃₋₂₀ alpha-olefin, obtained by polymerization with a metallocene compound as catalyst. The method of polymerization with a metallocene compound as catalyst refers to the method disclosed in, for example, republished International Publication No. WO95/15985.

[0013] Specifically, the method of polymerization with a metallocene compound as catalyst uses a catalyst containing constituents (I), (II) and (III) below. Constituent (I) is at least one type of transition metal compound represented by formula (1) below.

[0014]

Compound 1:



[0015] In the formula (1), M is a transition metal selected from a group consisting of zirconium, titanium and hafnium. R^1 is a ligand having a cyclopentadienyl backbone, or a C_{1-4} 5-member heterocyclic ligand containing nitrogen, phosphorus, arsenic, antimony or bismuth as heteroatom(s), or a heterotridentate ligand with nitrogen, phosphorus or oxygen occupying a coordinating position, wherein each ligand is either unsubstituted or is substituted by at least one substituent selected from a group consisting of a C_{1-20} alkyl group, a C_{6-20} aryl group, an aralkyl group wherein a C_{1-20} alkyl group is substituted with at least one C_{6-20} aryl group, and an alkylaryl group wherein a C_{6-20} aryl group is substituted with at least one C_{1-20} alkyl group. If substituted, substitution may occur on two or more parts of the ligand, and the alkyl group is linear, branched or cyclic, and at least one of said substituents may bind to the ligand via an oxygen, nitrogen or sulfur, and furthermore at least one of the carbons comprising the substituents may instead be a silicon.

[0016] R^2 , R^3 and R^4 are each independently a ligand having a cyclopentadienyl backbone, a C_{1-4} 5-member heterocyclic ligand containing nitrogen, phosphorus, arsenic, antimony or

bismuth as heteroatom(s), a heterotridentate ligand with nitrogen, phosphorus or oxygen occupying a coordinating position, a C₁₋₂₀ alkyl group, a C₆₋₂₀ aryl group, an aralkyl

/4

group wherein a C₁₋₂₀ alkyl group is substituted with at least one C₆₋₂₀ aryl group, an alkylaryl group wherein a C₆₋₂₀ aryl group is substituted with at least one C₁₋₂₀ alkyl group, -SO₃R (wherein R is a C₁₋₈ hydrocarbon group either unsubstituted or substituted with at least one halogen), a halogen atom, or a hydrogen atom. In the case of substitution, the alkyl group is linear, branched or cyclic, and the alkyl group, aryl group, alkylaryl group and alkaryl group may form a heteroatom ligand that binds to the transition metal via an oxygen, nitrogen, sulfur or phosphorus, and furthermore at least one of the carbons comprising the alkyl group, aryl group, alkylaryl group and alkaryl group may instead be a silicon. In addition, each respectively of the ligand having a cyclopentadienyl backbone, the C₁₋₄ 5-member heterocyclic ligand containing nitrogen, phosphorus, arsenic, antimony or bismuth as heteroatom(s), and the heterotridentate ligand with nitrogen, phosphorus or oxygen occupying a coordinating position are

either unsubstituted or substituted with at least one substituent selected from a group consisting of a C₁₋₂₀ alkyl group, a C₆₋₂₀ aryl group, an aralkyl group wherein a C₁₋₂₀ alkyl group is substituted with at least one C₆₋₂₀ aryl group, an alkylaryl group wherein a C₆₋₂₀ aryl group is substituted with at least one C₁₋₂₀ alkyl group. In the case of substitution, this may occur on two or more parts of the ligand, and the alkyl group is linear, branched or cyclic, and furthermore at least one of said substituents may bind to the ligand via an oxygen, nitrogen or sulfur, and at least one of the carbons comprising the substituents may be a silicon.

[0017] Symbol a is an integer of at least 1, and b, c and d are integers of 0 to 3, provided that a+b+c+d=4. R¹, R², R³ and R⁴ each bind to the transition metal M. R⁰ binds to R¹ and one selected from R², R³ and R⁴, and is a C₁₋₂₀ alkylene group, a C₁₋₂₀ alkylene group^(note 2), a C₁₋₂₀ alkylidene group, a silylene group, or a substituted silylene group substituted with at least one substituent selected from a group consisting of a C₁₋₂₀ alkyl group, a C₆₋₂₀ aryl group, an aralkyl group wherein a C₁₋₂₀ alkyl group is substituted with

² The repetition of this group appears to be an error in the original.

at least one C₆₋₂₀ aryl group, and an alkylaryl group wherein a C₆₋₂₀ aryl group is substituted with at least one C₁₋₂₀ alkyl group; and x is 0 or 1.

Constituent (II) is an inorganic solid constituent, wherein a fine powder inorganic solid (b-1) having a hydroxyl group on its surface supports:

[0018]

Compound 2:



[0019] the organoaluminum-oxy compound (b-2) having as its repeating unit an alkyloxy aluminum unit, as represented by formula (2) (wherein R⁶ is a linear, branching or cyclic C₁₋₁₂ alkyl group). Constituent (III) is an organoaluminum compound represented by formulas (3) or (4) below.

[0020]

Compound 3:



[0021] (In formula (3), R⁷ is a C₁₋₁₂ alkyl group, [or] a C₆₋₂₀ aryl group, X is a halogen or hydrogen, the alkyl group is linear, branched or cyclic and e is an integer from 1 to 3.)

[0022]

Compound 4:



[0023] (In formula (4), R^7 is the same as above, Y is an $-OR^8$ group, an $-OSiR^9_3$ group, an $-OAlR^{10}_2$ group, a $-NR^{11}_2$ group, a $-SiR^{12}_3$ group or a $-N(R^{13})AlR^{14}_2$ group; e is 1 or 2; R^8 , R^9 , R^{10} and R^{14} are each independently a C_{1-12} alkyl group or a C_{6-20} aryl group; R^{11} is hydrogen, a C_{1-12} alkyl group, a C_{6-20} aryl group, a silyl group, or a substituted silyl group substituted with at least one C_{1-12} alkyl group; and R^{12} and R^{13} are each independently a C_{1-12} alkyl group. The alkyl group in all above cases is linear, branched or cyclic.) Examples of the linear low-density ethylene copolymers (An) used for this invention include a linear low-density ethylene copolymer obtained by polymerization with the above metallocene compound as catalyst, and a linear low-density ethylene copolymer obtained by polymerization of an ethylene/1-octene copolymer (trade names Affinity and Engage) made by The Dow Chemical Company, with the metallocene compound as catalyst.

/5

[0024] The linear low-density ethylene copolymers (An) are random copolymers of a C₃₋₂₀ alpha-olefin and ethylene, obtained by polymerization with a metallocene compound as catalyst. Examples of the C₃₋₂₀ alpha-olefin copolymerized with ethylene include propylene, 1-butene, 1-pentene, 1-hexene, 1-octene, 1-decene, 1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene, 1-eicosene, 3-methyl-1-butene, 4-methyl-1-pentene, and 6-methyl-1-heptene.

[0025] The linear low-density ethylene copolymers (An) are obtained by polymerization using a metallocene compound as catalyst, and the linear low-density ethylene copolymer (A1) has a density of 0.87 g/cm³ or less. In addition, the melt flow rate is 0.1 to 40 g/10 min, and preferably 0.5 to 0.30g/10 min. A linear low-density ethylene copolymer which has these properties is preferred since it has good melting behavior and melt flow behavior, and exhibits low-temperature sealability, high heat sealing strength, and stable sealability over a wide temperature range.

[0026] The linear low-density ethylene copolymers (An-A1), which exclude linear low-density ethylene copolymer (A1), should have respectively different densities and melt flow rates. Density should exceed 0.87 g/cm³ and preferably range

from 0.88 to 0.94 g/cm³, and melt flow rate should be 0.1 to 40 g/10 min and preferably 0.5 to 30 g/10 min. Symbol n is preferably an integer from 1 to 5 and more preferably from 1 to 3.

[0027] Density was measured using a density gradient tube on a strand obtained when melt flow rate was measured under a 2.16 kg load at 190°C, the strand then being boiled in water for 1 hour and cooled at 23°C for 1 hour. Melt flow rate was measured under conditions of 190°C and a 2.16 kg load in accordance with ASTM D-1238. The low-density polyethylene (Bm) of this invention is one which can be obtained by known methods such as high-pressure radical polymerization. Symbol m is the integer 1 or 2.

[0028] The density of Bm is 0.91 to 0.93 g/cm³ and preferably 0.91 to 0.92 g/cm³. Melt flow rate is 0.1 to 10 g/10 min and preferably 0.3 to 5 g/10 min, and melt tension is at least 4 g. A low-density polyethylene with these properties has a considerable effect in improving neck-in of the extrusion laminate.

[0029] Melt tension was measured as the tension on a strand extruded under the same melt conditions as when melt flow rate was measured under a 2.16 kg load at 190°C, when drawn

at 785 cm/min. The density and melt flow rate of the low-density polyethylene were measured using the same methods as above. As with the low density polyethylene (B1), the low density polyethylene (B2) of this invention is one which can be obtained by a publicly known method such as high-pressure radical polymerization, and has a density of 0.91 to 0.93 g/cm³ and preferably 0.91 to 0.92 g/cm³. Melt flow rate is 1 to 30 g/10 min and preferably 1 to 20 g/10 min, and melt tension is less than 4 g, and preferably no more than 3 g. A low-density polyethylene with these properties exhibits a considerable effect in improving drawdown of the extrusion laminate.

[0030] The low-density polyethylenes (B1) and (B2) may be copolymers with, for example, other alpha-olefins, vinyl acetate or ester acrylate, as long as the objectives of this invention are still met. In the polyethylene resin composition for an extrusion laminate according to the first invention, the blending ratio of An is 50 to 99 wt.%, preferably 70 to 95 wt.%, and the blending ratio of Bm 50 to 1 wt.%, preferably 30 to 5 wt.%. If An is below this range, there may be deterioration of low-temperature heat sealability and seal strength, whereas if Bm is below the

above range, there may be insufficient improvement in neck-in and drawdown.

[0031] The blending ratio (weight ratio) $\{A1/(An-A1)\}$ of A1 and (An-A1) is 1/ 99 to 99/1 and preferably 5/95 to 90/10. If A1 is below this range, low-temperature sealability and stability sealability over a wide temperature range may not manifest. The blending ratio (weight ratio) $\{B1/B2\}$ of B1 and B2 is 1/ 99 to 99/1 and preferably 90/10 to 10/90. If the proportion of B1 is below this range there may be insufficient improvement of neck-in.

[0032] The polyethylene resin composition for an extrusion laminate according to the second invention must contain, relative to 100 parts weight of An and Bm combined, 0.01 to 0.5 parts weight, preferably 0.01 to 0.4 parts weight, of a phenolic heat stabilizer and/or phosphorus-based heat stabilizer, 0.01 to 0.2 parts weight, preferably 0.01 to 0.15 parts weight, of a slip agent, and 0.01 to 2 parts weight, preferably 0.01 to 1.5 parts weight, of an anti-blocking agent.

[0033] Examples of the phenolic heat stabilizer mentioned here include 2,6-di-t-butyl-4-methylphenol (dibutylhydroxytoluene), n-octadecyl-3-(4-

hydroxy-3,5-di-t-butylphenyl)propionate, and tetrakis(methylene(3,5-di-t-butyl-4-hydroxyhydrocinnamate)) methane. Examples of the phosphorus-based heat stabilizer include tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene-di-phosphonite. Examples of the slip agent include erucic acid amide, oleic acid amide, stearic acid amide and ethylene-bis-stearic acid amide. Examples of the anti-blocking agent include sodium calcium aluminosilicate and diatomaceous earth.

/6

[0034] If the phenolic heat stabilizer and or phosphorus-based heat stabilizer are below this range, during extrusion there may be heat degradation, adversely affecting melt flow properties and leading to deterioration in seal performance, whereas if this range is exceeded, problems such as discoloration may occur. If the slip agent and anti-blocking agent are below this range, slip properties during filling may be adversely affected and stable operation may become impossible, whereas if this range is exceeded there may be deterioration in seal performance.

[0035] This type of polyethylene resin composition for extrusion laminates according to this invention can be

manufactured using publicly known methods. For example, said polyethylene resin composition can be obtained by melt-kneading the linear low-density ethylene copolymers (An), low density polyethylenes (Bm) and additives such as the phenolic heat stabilizer, phosphorus-based heat stabilizer, slip agent and anti-blocking agent, using a single-screw extruder, a twin screw extruder or a kneader. Said additives can also be made as a master batch by blending with the low-density polyethylene and granulating by melt-kneading in a twin-screw extruder. Dry blends of these constituents can also be used to obtain said polyethylene resin composition.

[0036] For the extrusion laminate product according to the third invention, in the polyethylene resin composition for an extrusion laminate forming a sealant layer, temperature dependence of heat seal strength is 1.5 or less, heat seal strength is 1.5 kg/15 mm or more, the processability index of the extrusion laminate is 2 or more, and drawdown is 80 m/min or more. Temperature dependence of heat seal strength is a numerical value obtained by dividing the difference between the heat seal strength described below and the peel strength at a seal temperature of 90°C by the difference between complete heat seal temperature and 90°C,

then multiplying the result by 10; it expresses the temperature dependence of peel strength in the temperature range up to complete heat sealing, and the stability of heat sealability. If the temperature dependence of heat seal strength is greater than 1.5, it may be difficult to achieve stable heat sealability in response to fluctuations in seal temperature during filling, inviting the risk of deterioration in compression strength of filled receptacles. Furthermore, even when the temperature dependence of heat seal strength is 1.5 or less, if heat seal strength is below 1.5 kg/15 mm practical use may be difficult.

[0037] The processability index is the numerical value obtained by dividing drawdown by neck-in (at winding speed 60 m/min), both described below, and expresses productivity of the extrusion laminate. For example, a large processability index indicates that drawdown is large and so the extrusion laminate product can be produced more quickly, and/or that neck-in is small and so production can be achieved with a small amount of resin lost through trimming of edges. If the processability index is below 2, productivity of extrusion laminate processing will be poor and uneconomical even if low-temperature heat sealability

and seal strength are excellent. Moreover, even when the processability index is 2 or more, if drawdown is below 80 m/min, although excellent seal properties may well be obtained, productivity will be undesirably low.

[0038] As a substrate for the extrusion laminate product according to this invention, cellophane, nylon, polyethylene terephthalate, polypropylene, polyvinyl alcohol, aluminum foil, craft paper and so forth can be used independently or in a combination of two or more types. Moreover these substrates can be used as they are or with the application of a polyvinylidene chloride coating (so-called K-coat).

[0039] Furthermore, a substrate can be used wherein a low-density polyethylene, linear low-density polyethylene or linear low-density polyethylene obtained by polymerization with a metallocene compound as catalyst is laminated as a sandwich layer onto the aforementioned substrate either directly or by ozone treatment, using publicly known methods. The extrusion laminate product according to this invention can be obtained by extrusion lamination of a polyethylene resin composition for an extrusion laminate onto said substrate by publicly known methods.

[0040]

EMBODIMENTS OF THE INVENTION: The invention is described in further detail below using embodiments. The polymers, extrusion lamination methods and methods for measuring physical properties are as below.

(1) Linear low-density ethylene copolymers (An): Ethylene/1-octene copolymers were used. For the metallocene compound catalyst used in polymerization to obtain said copolymers, (n-butylcyclopentadienyl)zirconium chloride or ethylene bis(indenyl)zirconium dichloride was used, methylaluminoxane supported on porous silica was used as the organoaluminum-oxy compound, and triisobutylaluminum was used as the organoaluminum compound. The quantitative ratio of metallocene compound to organoaluminum-oxy compound was set to 1:500 (mole ratio) in zirconium and aluminum equivalents, and the quantitative ratio of an organoaluminum-oxime^(note 3) compound to organoaluminum compound was set to 63:37 (mole ratio) as aluminum equivalent.

[0041] For the catalyst preparation solvent, toluene was used as the solvent in supporting methylaluminoxane on the porous silica. Polymerization was carried out at 70°C under

³ 'oxime' may be a spelling mistake in the original, and should perhaps be 'oxy'.

pressure of 7 kg/cm²G. The linear low-density ethylene copolymer (A1) and the linear low-density ethylene copolymers (An-A1) excluding A1 were obtained with densities and melt flow rates altered depending on some of the conditions set in the above polymerization method, such as amount of 1-octene, type of silica, type and amount of metallocene compound, and polymerization temperature.

/7

[0042] In addition, in the embodiments and comparison examples, an ethylene/1-octene copolymer (made by The Dow Chemical Company, trade name Engage EG8200) was used as a linear low-density ethylene copolymer (A1), and ethylene/1-octene copolymers (made by The Dow Chemical Company, trade names Affinity PT1450, Affinity HM1100 and Affinity SM1300) were used as the linear low-density ethylene copolymers (An-A1) excluding A1.

(2) Low density polyethylene (B1), low-density polyethylene (B2): Low-density polyethylenes obtained by high-pressure radical polymerization were used.

(3) Master batch (C): Low density polyethylene was blended with n-octadecyl-3-(4-hydroxy-3,5-di-t-butylphenyl)propionate as phenolic heat stabilizer,

tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene-di-phosphonite as phosphorus-based heat stabilizer, erucic acid amide as slip agent and sodium calcium aluminosilicate as anti-blocking agent, then granulated by melt-kneading with a twin screw extruder.

(4) Extrusion lamination method: A single screw extruder provided with a straight manifold die was used, with lip width set to 400 mm and lip clearance set to 0.7 mm. The resin was extruded at resin temperature 300°C, passed through a 140 mm air gap and laminated onto a substrate fed out from a feeder. After this, the laminated product was cooled on a semi-mirror-finished chill roll and wound up on a winder.

[0043] The substrate used was one obtained by treating ONy (25 μm) with an anchoring agent, then laminating in advance a low-density polyethylene with density 0.923 g/cm³ and melt flow rate 4.0 to a thickness of 20 μm using the above method.

(5) Measurement of physical properties

1) Neck-in: The method was the same as in the above extrusion lamination method, except in the use of craft paper given 2 kw corona treatment as substrate, and winding speed was increased from 60 m/min to 120 m/min with the

discharge amount fixed to an amount which gave a laminate thickness of 20 μm at a winding speed of 60 m/min. Neck-in (mm) was defined as the sum of the neck-in distance from both edges.

2) Drawdown: Speed when neck-in was measured and speed at which surging began or film-tear occurred when winding speed was increased were evaluated as drawdown (m/min).

3) Processability index of extrusion laminate: The numerical value obtained by dividing drawdown (m/min) by neck-in (mm) at winding speed 60 m/min was taken as processability index of the extrusion laminate.

4) Heat seal strength: Using a heat sealer (made by Tester Sangyo Co. Ltd), the laminate product obtained by the above extrusion lamination method was heat-sealed at a seal pressure of 2 kg/cm² for a seal time of 1 second, with seal temperature being increased in 10°C increments from 80°C. Using a tensile tester (made by Orientec Co. Ltd), peel strength of the seal was measured under a tension rate of 500 mm/min, and heat seal strength was taken as the value when peel strength reached equilibrium.

5) Low-temperature heat-sealability: The temperature at which the above heat seal strength was achieved was taken as

complete heat seal strength and used as a scale for low-temperature heat-sealability.

6) Temperature dependence of heat seal strength: Temperature dependence of heat seal strength was defined as the numerical value obtained by dividing the difference between the above heat seal strength and peel strength at seal temperature 90°C by the difference between complete heat seal temperature and 100°C^(note 4) and multiplying the result by 10. When sealing was not achieved at 90°C, peel strength was taken to be 0 kg/15 mm.

7) Slip: This was measured using the laminate product obtained by the above extrusion lamination method. Using a slip angle tester (made by Toyo Seiki Seisakusho), a metal indenter with weight adjusted so as to give a surface pressure of 7.6 g/cm² was placed on the sealant layer constituted by the laminate product. The angle of inclination was gradually raised and the angle at which the indenter began to slip was measured as the slip angle. In this way slip was evaluated.

⁴ '100' may be a mistake in the original, and should perhaps be '90'.

[0044]

EMBODIMENT 1: Of the two or more types of linear low-density ethylene copolymer, one type (A1) was an ethylene/1-octene copolymer obtained by the above polymerization method, with a density of 0.868 g/cm^3 and melt flow rate of 5.1 g/10 min . For the linear low-density ethylene copolymer(s) (An-A1) which excludes (A1), an ethylene/1-octene copolymer (A2) obtained by the above polymerization method, with a density of 0.902 g/cm^3 and melt flow rate of 8.1 g/10 min , was used.

[0045] In addition, the low density polyethylene (B1) had a density of 0.918 g/cm^3 , melt flow rate of 2.0 g/10 min and melt tension of 8.4 g , whereas low density polyethylene (B-2) had a density of 0.916 g/cm^3 , melt flow rate of 4.2 g/10 min and melt tension of 3.5 g . Blending rates were set at 80% An and 20% Bm, the blending ratio (weight ratio) of A1/(An-A1) was 25/75, and the blending ratio (weight ratio) of (B1/B2) was 75/25.

[0046] A master batch (C) was further mixed, prepared as a dry blend, then granulated by melt-kneading in a single screw extruder. The obtained polyethylene resin composition was thus compounded with additives in the form of 2000 ppm n-octadecyl-3-(4-hydroxy-3,5-di-t-butylphenyl)propionate,

1000 ppm tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene-di-phosphonite, 500 ppm erucic acid amide and 3000 ppm sodium calcium aluminosilicate. Using the resultant polyethylene resin composition, extrusion lamination was carried out by the above method and processability was evaluated. In addition, the resultant laminate product was evaluated for heat seal strength, low-temperature sealability and slip. Table 1 shows resin compositions and Table 2 shows processability, heat seal strength, low-temperature sealability, temperature dependence of heat seal strength, and slip.

/8

[0047]

EMBODIMENTS 2 and 3: Apart from changing the density and melt flow rate of the linear low-density ethylene copolymer (A2), the same method as embodiment 1 was used for granulation and extrusion coating, evaluation of processability, and evaluation of the resultant laminate product for heat seal strength and slip. Table 1 shows resin compositions and Table 2 shows processability, heat seal strength, low-temperature sealability, temperature

dependence of heat seal strength and slip, together with those of embodiment 1.

[0048]

EMBODIMENT 4: For the linear low-density ethylene copolymer (A1), Engage EG8200 (trade name for ethylene/1-octene copolymer) made by The Dow Chemical Company was used, and for the linear low-density ethylene copolymer (A2), Affinity PT1450 (trade name for ethylene/1-octene copolymer) made by The Dow Chemical Company was used. Using the same method as embodiment 1, extrusion lamination was carried out and processability was evaluated. In addition the resultant laminate product was evaluated for heat seal strength, low-temperature sealability and slip. Table 1 shows resin compositions and table 2 shows processability, heat seal strength, low-temperature sealability, temperature dependence of heat seal strength and slip.

[0049]

EMBODIMENT 5: For the linear low-density ethylene copolymer (A2), Affinity HM1100 (trade name for ethylene/1-octene copolymer) made by The Dow Chemical Company was used. Apart from this, the same method as Embodiment 4 was used for extrusion lamination, evaluation of processability, and

evaluation of the resultant laminate product for heat seal strength, low-temperature sealability and slip. Table 1 shows resin compositions and Table 2 shows processability, heat seal strength, low-temperature sealability, temperature dependence of heat seal strength and slip.

[0050]

EMBODIMENTS 6 and 7: In addition to those used in Embodiment 4, Affinity SM1300 (trade name for ethylene/1-octene copolymer) made by The Dow Chemical Company was further used for the linear low-density ethylene copolymer (A3), and the blending rate of An and Bm, the blending ratio (weight ratio) of A1/(An-A1) and the blending ratio (weight ratio) of B1/B2 were changed. The same method as Embodiment 4 was then used for extrusion lamination, evaluation of processability, and evaluation of the resultant laminate product for heat seal strength, low-temperature sealability and slip. Table 1 shows resin compositions and Table 2 shows processability, heat seal strength, low-temperature sealability, temperature dependence of heat seal strength and slip.

Table 1

			Embodiment						
			1	2	3	4	5	6	7
Linear low-density ethylene copolymer	A1	Density (g/cm ³)	0.868	-	0.868	0.870	0.870	0.870	0.870
		Melt flow rate (g/10min)	5.1	5.1	5.1	5.0	5.0	5.0	5.0
	A2	Density (g/cm ³)	0.902	0.895	0.913	0.903	0.880	0.903	0.903
		Melt flow rate (g/10min)	8.1	10.0	18.0	7.5	18.0	7.5	7.5
	A3	Density (g/cm ³)	-	-	-	-	-	0.902	0.902
		Melt flow rate (g/10min)	-	-	-	-	-	30.0	30.0
Low density polyethylene	B1	Density (g/cm ³)	0.918	0.918	0.918	0.918	0.918	0.918	0.918
		Melt flow rate (g/10min)	2.0	2.0	2.0	2.0	2.0	2.0	2.0
		Melt tension (g)	8.4	8.4	8.4	8.4	8.4	8.4	8.4
	B2	Density (g/cm ³)	0.916	0.916	0.916	0.916	0.916	0.916	0.916
		Melt flow rate (g/10min)	4.2	4.2	4.2	4.2	4.2	4.2	4.2
		Melt tension (g)	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Blending ratio	An (wt.%)		80	80	80	80	80	85	70
	Bm (wt.%)		20	20	20	20	20	15	30
	A1/(An-A1) (wt. ratio)		25/75	25/75	25/75	25/75	25/75	18/82	18/82
	A2/A3 (wt. ratio)		-	-	-	-	-	67/33	67/33
	B1/B2 (wt. ratio)		75/25	75/25	75/25	75/25	75/25	50/50	50/50
Additives	n-octadecyl-3-(4-hydroxy-3,5-di-t-butylphenyl)propionate (ppm)		2000	2000	2000	2000	2000	2000	2000
	Tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene-di-phosphonite (ppm)		1000	1000	1000	1000	1000	1000	1000

	Erucic acid amide (ppm)	500	500	500	500	500	500	500
	Sodium calcium aluminosilicate (ppm)	3000	3000	3000	3000	3000	3000	3000

[0052]

/10

Table 2

			Embodiment						
			1	2	3	4	5	6	7
Processability	Drawdown (m/min)		160	170	170	150	150	170	160
	Neck-in (mm)	60 (m/min)	71	73	72	71	74	73	68
		80 (m/min)	60	61	61	61	64	60	59
		100 (m/min)	55	56	56	56	60	55	54
		120 (m/min)	52	53	53	54	58	52	51
	Processability index		2.25	2.33	2.36	2.11	2.03	2.33	2.35
Seal properties	Heat seal strength (kg/15mm)		4.92	4.50	4.51	5.00	4.00	4.60	4.30
	Complete seal temp. (°C)		120	120	120	120	120	120	120
	Temperature dependence of heat seal strength		1.14	1.00	1.00	1.17	0.83	1.03	0.92
Slip angle (deg)			28	27	27	29	30	28	27

[0053] As is clear from Tables 1 and 2, the polyethylene resin composition for an extrusion laminate according to this invention has excellent processability characteristics such as neck-in and drawdown as an extrusion coating, exhibits low-temperature heat sealability, high heat seal strength and stable heat sealability, as well as having good

slip, and is thus ideal as a resin composition for an extrusion coating for use as a sealant layer.

[0054]

COMPARISON EXAMPLES 1 to 4: Table 3 shows the composition of the polyethylene resin compositions used in these comparison examples, and Table 4 shows processability, heat seal strength, low-temperature sealability, temperature dependence of heat seal strength and slip in each comparison example.

[0055]

COMPARISON EXAMPLES 5 to 7: For the linear low-density ethylene copolymer (A1), Engage EG8200 made by The Dow Chemical Company (trade name of ethylene/1-octene copolymer) was used. For the linear low-density ethylene copolymers (An-A1) which exclude A1, Affinity PT1450 (trade name for ethylene/1-octene copolymer) made by The Dow Chemical Company was used as A2, and Affinity SM1300 (trade name for ethylene/1-octene copolymer) made by The Dow Chemical Company was further used as linear low-density ethylene copolymer A3. Table 3 shows the composition of these polyethylene resin compositions, and Table 4 shows their processability, heat seal strength, low-temperature

sealability, temperature dependence of heat seal strength and slip.

[0056]

/11

Table 3

			Comparison example						
			1	2	3	4	5	6	7
Linear low-density ethylene copolymer	A1	Density (g/cm ³)	0.868	0.868	0.868	0.868	0.870	0.870	0.870
		Melt flow rate (g/10min)	5.1	-	5.1	5.1	5.0	5.0	5.0
	A2	Density (g/cm ³)	-	0.902	0.902	0.902	0.903	0.903	0.903
		Melt flow rate (g/10min)	-	8.1	8.1	8.1	7.5	7.5	7.5
	A3	Density (g/cm ³)	-	-	-	-	0.902	0.902	0.902
		Melt flow rate (g/10min)	-	-	-	-	30.0	30.0	30.0
Low density polyethylene	B1	Density (g/cm ³)	0.918	0.918	0.918	0.918	0.918	0.918	0.918
		Melt flow rate (g/10min)	2.0	2.0	2.0	2.0	2.0	2.0	2.0
		Melt tension (g)	8.4	8.4	8.4	8.4	8.4	8.4	8.4
	B2	Density (g/cm ³)	0.916	0.916	0.916	0.916	0.916	0.916	0.916
		Melt flow rate (g/10min)	4.2	4.2	4.2	4.2	4.2	4.2	4.2
		Melt tension (g)	3.5	3.5	3.5	3.5	3.5	3.5	3.5
Blending ratio	An (wt.%)		80	80	40	80	40	100	85
	Bm (wt.%)		20	20	60	20	60	0	15
	A1/(An-A1) (wt. ratio)		25/75	25/75	25/75	25/75	25/75	18/82	18/82
	A2/A3 (wt. ratio)		-	-	-	-	67/33	67/33	67/33
	B1/B2 (wt. ratio)		75/25	75/25	75/25	0/100	50/50	-	50/50
Additives	n-octadecyl-3-(4-hydroxy 3,5-di t-butylphenyl)propio		2000	2000	2000	2000	2000	2000	2000

	nate (ppm)							
	Tetrakis(2,4-di-t-butylphenyl)-4,4'-biphenylene-di-phosphonite (ppm)	1000	1000	1000	1000	1000	1000	1000
	Erucic acid amide (ppm)	500	500	500	500	500	500	50
	Sodium calcium aluminosilicate (ppm)	3000	3000	3000	3000	3000	3000	50

[0057]

/12

Table 4

			Comparison example						
			1	2	3	4	5	6	7
Processability	Drawdown (m/min)		90	160	90	170	165	150	160
	Neck-in (mm)	60 (m/min)	182	69	50	77	72	127	79
		80 (m/min)	175	58	48	63	60	118	70
		100 (m/min)	-	53	-	54	56	108	67
		120 (m/min)	-	50	-	51	55	102	64
	Processability index		0.49	2.32	1.80	2.21	2.29	1.18	2.03
Seal properties	Heat seal strength (kg/15mm)		1.65	5.28	3.65	5.10	3.78	4.97	4.45
	Complete seal temp. (°C)		100	120	140	120	140	120	120
	Temperature dependence of heat seal strength.		1.50	1.76	0.73	1.70	0.76	1.65	0.95
Slip angle (deg)			≥60	29	2?	28	24	32	58

[0058]

EFFECTS OF THE INVENTION: Compared to the prior art, the polyethylene resin composition for an extrusion laminate according to this invention has excellent processability characteristics such as neck-in and drawdown as an extrusion

laminate, exhibits low-temperature heat sealability, high heat seal strength and stable heat sealability, as well as having good slip, and is thus ideal as a resin composition for an extrusion coating for use as a sealant layer.

[0059] In addition, the extrusion laminate product according to this invention, which uses said resin for a sealant layer, has high productivity, as well as excellent suitability for high speed filling due to having low temperature heat sealability, high heat seal strength, stable heat sealability and good slip, and can favorably be used as a packaging material for foodstuffs such as soups, liquids, pastes, meats, processed meat products, etc.